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Die angehefteten Stücke sind eine richtige und genaue Wiedergabe der ursprünglichen Unterlagen dieser Patentanmeldung.

München, den 22. Juli 2004
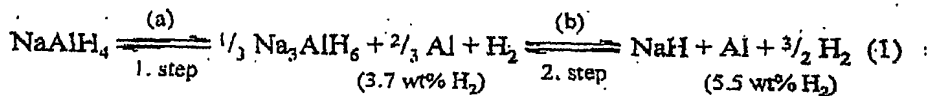**Deutsches Patent- und Markenamt**
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Abstract

High dispersion of hydrogen storage material can be achieved by encapsulating the material in highly porous solid matrices.

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Materials encapsulated in porous matrices for the reversible storage of hydrogen

High dispersion of hydrogen storage material can be achieved by encapsulating the material in highly porous solid matrices.

Suitable means for hydrogen storage are one of the key requirements for hydrogen fuel cell technology (State-of-the-art review on hydrogen storage is presented in a special issue of the Materials Research Society Bulletin, September 2002). Physical methods, such as compression or liquefaction, are viable solutions, but they have severe disadvantages, such as the need for high pressures in order to achieve sufficiently high storage densities, or the need for cryogenic systems to overcome evaporation losses.

An alternative is storing hydrogen in the form of hydrides. However, not many hydrides are suitable for this, due to either too high or too low decomposition temperatures, insufficient gravimetric of volumetric storage capacity, or irreversibility of hydrogen release. It was therefore considered a very significant invention that $NaAlH_4$ can be used as a reversible hydrogen storage material (Equations 1a,b); alone and especially when doped with transition or rare earth metal catalysts, in particular titanium (SGK, PCT/WO 97/03919, PCT/EP01/02363 and DP 10163697.0).

$$ NaAlH_4 \underset{1.\,step}{\overset{(a)}{\rightleftharpoons}} \,^1/_3\, Na_3AlH_6 + \,^2/_3\, Al + H_2 \underset{2.\,step}{\overset{(b)}{\rightleftharpoons}} NaH + Al + \,^3/_2\, H_2 \quad (1) $$
$$ (3.7\ wt\%\ H_2) \qquad\qquad (5.5\ wt\%\ H_2) $$

However, at present, these materials still have several shortcomings, among them especially

- the kinetics of hydrogen dis- and recharging needs to be further improved; this is especially valid for the recharging rate, which should be in the order of several minutes;
- safety aspects, due to the pyrophoric nature of doped alanates, are not yet solved;
- thermodynamic properties of doped alanates have to be adjusted to the requirements given by the temperature of the waste heat of fuel cell cars (~ 100 °C).

Surprisingly, it has now been found that these problems can be partially or largely obviated, if the storage material is dispersed inside of very small compartments (encapsulation), which

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are present in many kinds of materials, i. e. highly porous materials. Particularly suitable for encapsulation, especially of light metal hydrides, are found to be highly porous matrices such as aerogels of silica, carbon or meso-structured carbons (CMK-1, -2, -3, -4, -5), or xerogels of the same materials, or other kinds of porous matrices, such as zeolites and porous metal frame works (as described by Yaghi).

Encapsulation in general, as exemplified by the metal hydrides for hydrogen storage materials, leads to high dispersion of the material with the following three effects:

1. Kinetics is improved, since mass transfer distances are minimized;
2. Thermodynamics are altered, since large surface effects of nanosized powders can lead to additional energetic contribution, which is in favorable cases destabilization;
3. The incorporation leads to hindered access of air and moisture and thus to improved safety.

As materials for encapsulation metal hydrides, e. g. alanates, can be used, e. g. sodium alanate ($NaAlH_4$). Other useful materials for encapsulation are mixtures of aluminium metal with alkali metal or alkali metal hydride and with a catalyst comprising a compound of a transition metal or of a rare earth metal or this metal in elemental form. Preferably Ti is used as transition metal. Other materials for encapsulation are MgH_2 or MgH_2 doped with transition metals (e. g. Ti) or transition metal compounds.

Such encupsulated materials, e. g. light metal hydrides encapsulated in highly porous matrices, can be applied as hydrogen storage materials, for instance for supplying fuel cell systems of fuel cell vehicles with hydrogen, with advantages described above.

As described in Examples 1 and 2 the encapsulation of Ti doped sodium alanate in porous carbon (specified by the data given in examples) is carried out by successively impregnating the porous carbon with solutions of the doping agent ($TiCl_4$) and $NaAlH_4$ in organic solvents, e. g. toluene, and subsequent removal of organic solvents in vacuum.

The encapsulated Ti doped $NaAlH_4$ shows the ability in cycle tests to be reversibly de- and recharged with hydrogen under the same conditions as the non-encapsulated Ti doped $NaAlH_4$ (Table 1). However, as it can be seen by comparison of Figs. 1 and 2 with the Fig. 3, the encapsulated Ti doped $NaAlH_4$ reveals a higher hydrogen desorption rate than the non-encapsulated one. So, for examples, the encapsulated Ti doped $NaAlH_4$ (Fig. 1) at 120 °C is

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discharged to the extent of 80 % in only 30-40 min, while the non-encapsulated Ti doped NaAlH₄ (Fig. 3) at the same temperature requires 2 ½ h to desorb 80 % of stored hydrogen.

Decomposition of NaAlH₄ is in several steps. After NaH, Al and H₂ are generated, in the final step NaH is further decomposed to Na and H₂. Due to the higher dispersion of the materials thermodynamics are altered; the process is carried out at lower temperatures. (Fig. 4)

In addition, as shown in Fig. 5, in contrast to the non-encapsulated Ti doped NaAlH₄, the encapsulated Ti doped NaAlH₄ does not ignite on air.

For illustration of the invention serve the following examples 1 and 2.

Example 1

Preparation of porous carbon: Porous carbon was prepared essentially following the recipe described in *J. Non.-Cryst. Solids 1997, 221, 144*. Accordingly, resorcinol (19.4g) was copolymerized with formaldehyde in water (68 ml) in the presence of sodium carbonate as a base (molar ratio: $1:2:7:7 \cdot 10^{-4}$). The solution was kept 24 h at room temperature, 24 h at 50°C and finally 72 h at 90°C. The thus obtained aqueous gel was cut in pieces and suspended in acetone in order to exchange water in the pores against acetone. Every day in the course of 7 days the solution was decanted from the solid and fresh acetone was added. The obtained resorcinol – formaldehyde copolymer was evacuated, placed in quartz tube and then in argon stream, heated for 0.5 h to 350°C and for 2.5 h to 1000°C. After cooling down to room temperature, the porous carbon was ground to a powder in an agate mortar. The thus obtained porous carbon (5.16g), according to nitrogen sorption measurements, had a pore volume of 0.55 cm³/g, pore diameter of 22.6 nm and a surface area of 553.9 m³/g.

Preparation of Ti-doped NaAlH₄ encapsulated in porous carbon: 2.2885g of porous carbon was evacuated for 3 h at 500°C. After cooling down to room temperature, porous carbon was impregnated with a TiCl₄/toluene (1/10, v/v) solution using the incipient wetness method and then the solvent removed by evacuation in vacuum. The weight of the sample increased to 2.6999g, corresponding to 0.4114g of supported TiCl₄. Subsequently the sample was impregnated in the same way with a 2 M solution of NaAlH₄ in tetrahydrofurane. The weight of the sample increased to 4.4489g indicating 1.7490g of supported NaAlH₄. As known, TiCl₄ reacts with NaAlH₄ under reduction to elemental titanium according to the following reaction;

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$$TiCl_4 + 4NaAlH_4 \longrightarrow Ti + 4NaCl + 4Al + 8H_2 \uparrow$$

Accordingly, the composition of the Ti doped $NaAlH_4$ encapsulated in porous carbon is: porous carbon, 2.2885g; Ti, 0.1039g; $NaAlH_4$, 1.280g; NaCl, 0.5069g. This composition corresponds to the $NaAlH_4$ loading level of 30.6 wt % and to doping level of Ti in $NaAlH_4$ of 8.3 mole %. Assuming the density of $NaAlH_4$ were 1.28g/cm^3 and of NaCl 2.20 g/cm^3, the pore occupancy of the carbon matrix of 98% was ulated.

Example 2

Preparation of porous carbon was carried out in the same way as in Example 1, except that the amount of Na_2CO_3 was doubled. Properties of the porous carbon of the Example 2, according to nitrogen sorption measurements: pore volume 0.98 cm^3/g, pore diameter 15.3 nm, surface area 578.2 m^2/g. According to the composition of encapsulated Ti doped $NaAlH_4$, the loading level of $NaAlH_4$ in the matrix was 48.9 wt % and the doping level of Ti in $NaAlH_4$ 3.9 mole %. On the basis of the assumed $NaAlH_4$ and NaCl densities, a pore occupancy of 104 % was calculated.

Hydrogen de- and reabsorption measurements of Ti doped NaAlH$_4$ encapsulated in porous carbon: Hydrogen desorptions were measured by heating in a thermovolumetric apparatus 1-1.2g sample successively to 120 and 180°C (4 °C/min) and keeping temperature at the two levels constant until the end of hydrogen desorption. Hydrogen reabsorptions were carried out at 100°C/100 bar for 24 h in an autoclave.

TG-DTA measurements were perfomed under Ar flow (100 mL/min) with the temperature ramp rate of 2 °C/min. for encapsulated Ti dopped $NaAlH_4$ (Example 2) or for 4 °C/min. for non- encapsulated Ti dopped $NaAlH_4$. (Fig. 4)

Hydrogen storage capacities achieved in cycle tests (hydrogen de- and reabsorption measurements) of the Examples 1 and 2 are given in Table 1, and the hydrogen desorption curves illustrated by Figs. 1 and 2. For comparison, a cycle test (Table 1 and Fig. 3) under the same conditions was carried out also with a sample of non-encapsulated Ti doped $NaAlH_4$, prepared by doping of $NaAlH_4$ with $TiCl_4$ in toluene, as described in *J. Alloys Comp. 2000, 302, 36.*

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Table 1.

Hydrogen storage capacities of encapsulated versus non-encapsulated Ti doped $NaAlH_4$ (in the Examples 1 and 2, wt % of hydrogen are normalized to $NaAlH_4$ only [a])
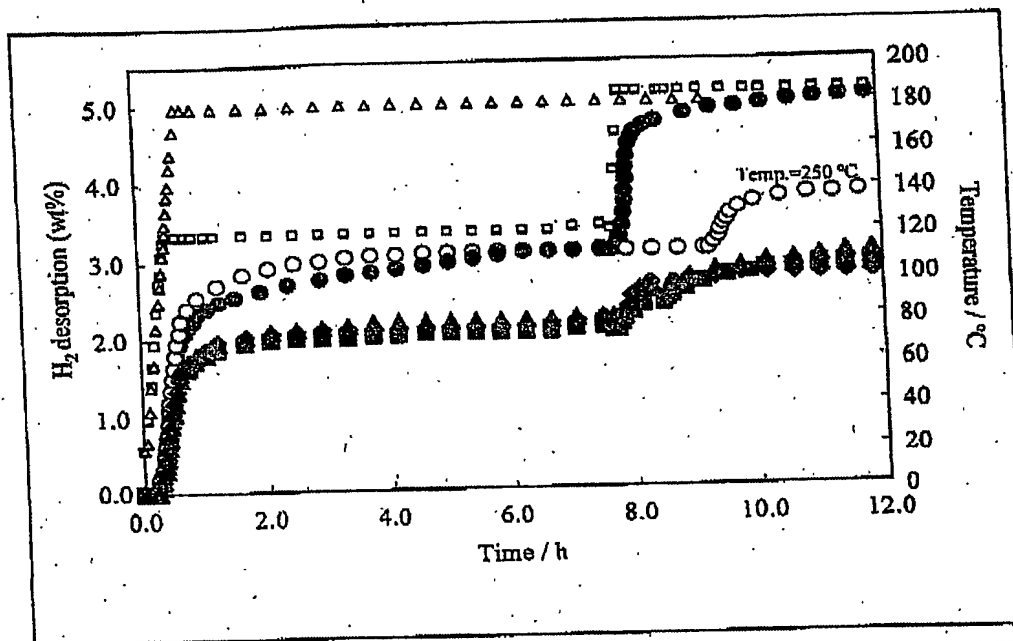
Cycle number	Example 1		Example 2		Non encapsulated Ti doped $NaAlH_4$	
	120 °C	total capacity (180 °C)	120 °C	total capacity (180 °C)	120 °C	total capacity (180 °C)
1	3.06(0.88)	5.16(1.48)			2.32	3.70
2	2.17(0.62)	3.16(0.91)	1.55(0.60)	3.36(1.31)	0.90	1.58
3	2.03(0.58)	2.86(0.82)	1.59(0.62)	2.53(0.98)		
4	-	3.04(0.88)	1.70(0.66)	2.97(1.16)		
5	2.11(0.61)	3.12(0.90)				

[a] The values given in parenthesis are in terms of wt % H_2 with respect to overall weight of samples.

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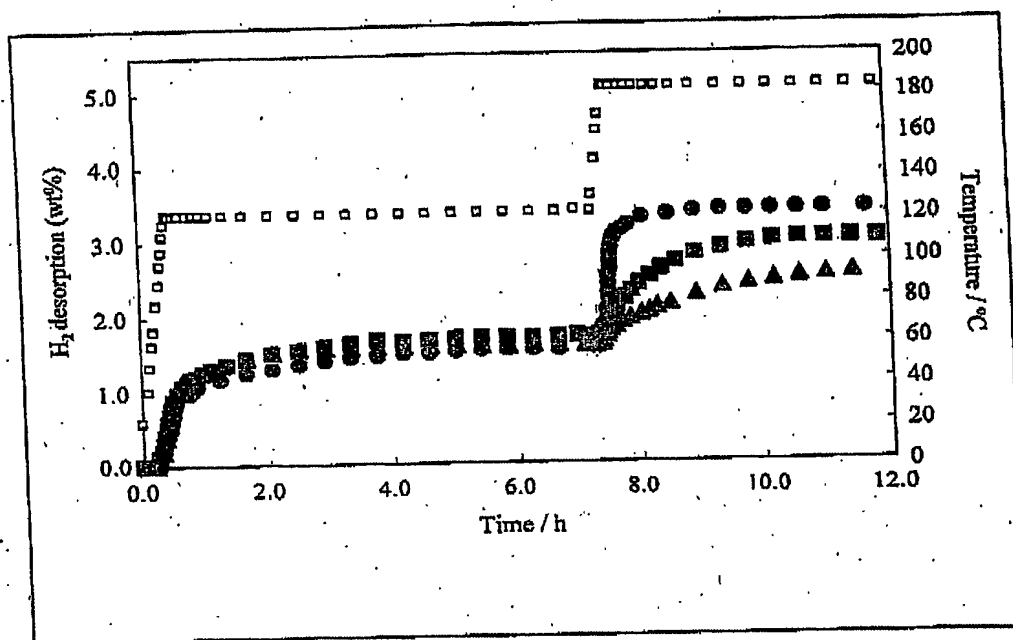Betreff: 12 Seite(n) empfangen

Claims:

1. Material, comprising

   sodium alanate,

   or a mixture of aluminum metal with alkali metal or alkali metal hydride and with a transition metal or rare-earth metal catalyst;

   or magnesium hydride, preferable doped with a transition metal or a transtion metal compound,

   encapsulated in a porous solid matrix.

2. Material according to claim 1, wherein said transition metal is titanium.

3. Material according to claims 1, wherein said porous matrix is porous carbon.

4. Material according to claims 1, wherein said porous matrix is mesostructured carbon.

5. Material according to claims 1, wherein said porous matrix is carbon xerogel.

6. Material according to claims 1, wherein said porous matrix is silica aerogel.

7. Material according to claims 1, wherein said porous matrix is silica xerogel.

8. Material according to claims 1, wherein said porous matrix is zeolite.

9. Material according to claims 1, wherein said porous matrix comprises porous metal frame works

10. Process for the preparation of material of claim 1 comprising impregnating the porous matrix with a solution of said material in an organic solvent.

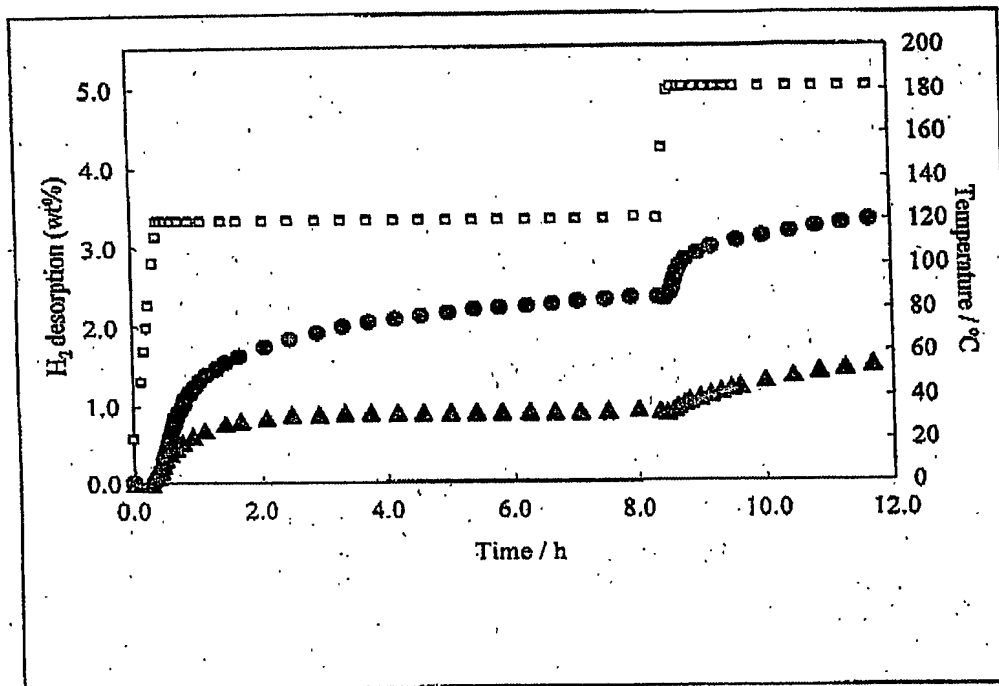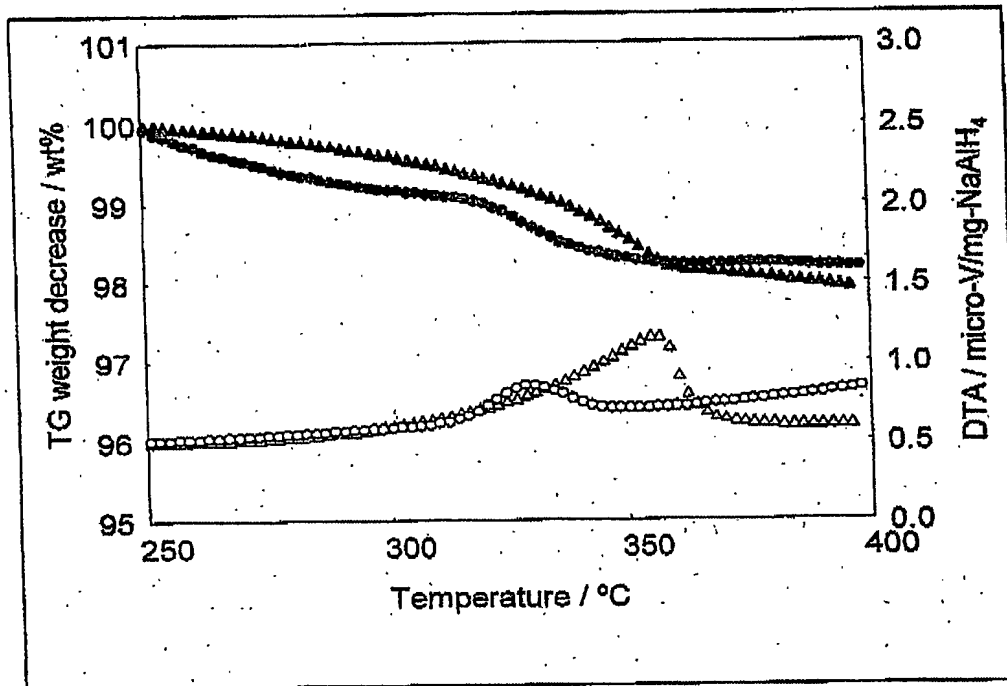11. Use of material of claim 1-7 as hydrogen storage material.

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Encapsulated Tl doped NaAlH$_4$ (Example 1); (●) cycle 1, (▲) cycle 2, (■) cycle 3, (○) cycle 4, (♦) cycle 5; (□) temperature cycles 1-3 and 5; (Δ) temperature cycle 4.
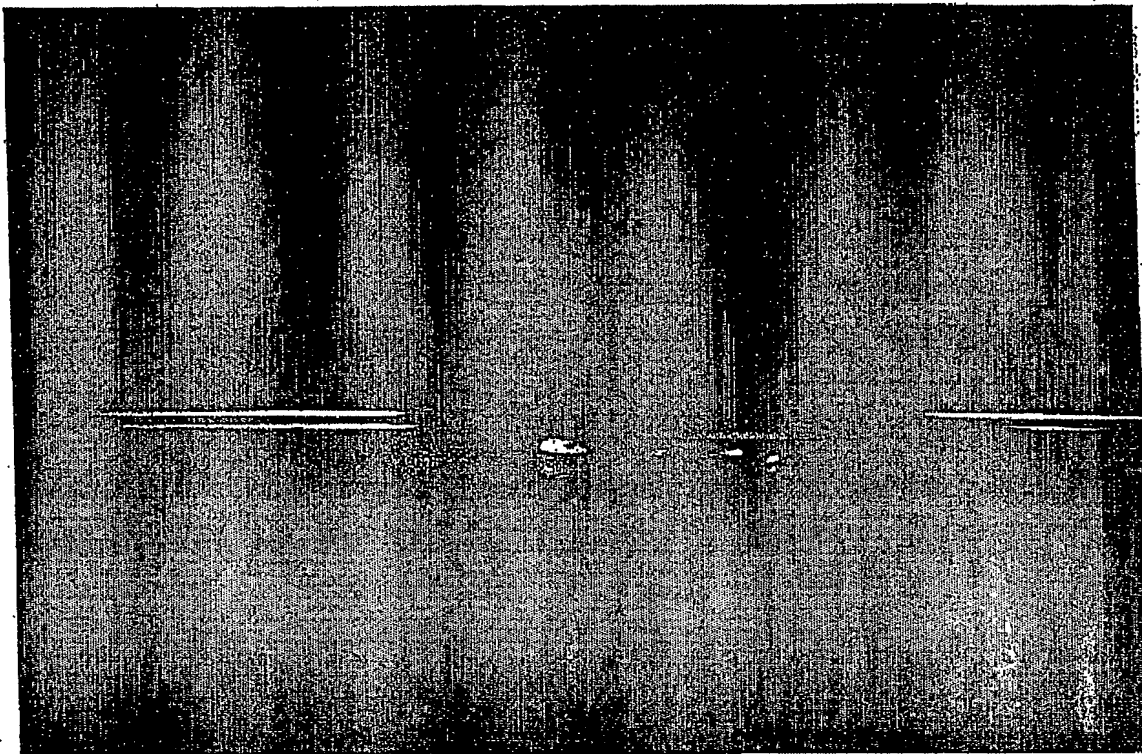
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Encapsulated Ti doped NaAlH₄ (Example 2); (●) cycle 1, (▲) cycle 2, (■) cycle 3,; (□) temperature cycles 1-3.

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Non-encapsulated Tl doped NaAlH₄; (●) cycle 1, (▲) cycle 2,; (□) temperature
cycles 1 and 2.

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TG-DTA of encapsulated and non-capsulated Ti doped NaAlH₄; (●) TG of encapsulated Ti doped NaAlH₄ (Example 2), (▲) TG of non capsulated Ti doped NaAlH₄, (○) DTA of Ti doped NaAlH₄ (Example 2), (△) DTA of non capsulated Ti doped NaAlH₄.

NaAlH4 doped with Tl after contact with air:
upper probe is encapsulated, lower is non-ecupsulated. (Example 1)

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